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Review and experimental study on pyrolysis and hydrothermal liquefaction of microalgae for biofuel production

David Chiaramonti [a,*], Matteo Prussi [a], Marco Buffi [a], Andrea Maria Rizzo [a], Luigi Pari [b]

[a] *Renewable Energy COnsortium for R&D, RE-CORD c/o Department of Industrial Engineering, School of Engineering, University of Florence, Viale Morgagni 40, I-50134 Florence, Italy*
[b] *Consiglio per la Ricerca in Agricoltura e l'Analisi dell'Economia Agraria, Unità di Ricerca per l'Ingegneria Agraria, Rome, Italy*

HIGHLIGHTS

- A review of microalgae thermochemical conversion to bioliquids was carried out.
- We focused on pyrolysis and hydrothermal liquefaction for biocrude/biofuels.
- Original experimental research on microalgae pyrolysis was also carried out.
- Starvation does not impact significant on the energy content of the biocrude.
- This result is relevant for designing full scale microalgae production plants.

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ABSTRACT

Advanced Biofuels steadily developed during recent year, with several highly innovative processes and technologies explored at various scales: among these, lignocellulosic ethanol and CTO (Crude Tall Oil)-biofuel technologies already achieved early-commercial status, while hydrotreating of vegetable oils is today fully commercial, with almost 3.5 Mt/y installed capacity worldwide. In this context, microalgae grown in salt-water and arid areas represent a promising sustainable chain for advanced biofuel production but, at the same time, they also represent a considerable challenge. Processing microalgae in an economic way into a viable and sustainable liquid biofuel (a low-cost mass-product) is not trivial. So far, the most studied microalgae-based biofuel chain is composed by microorganism cultivation, lipid accumulation, oil extraction, co-product valorization, and algae oil conversion through conventional esterification into Fatty Acids Methyl Esters (FAME), i.e. Biodiesel, or Hydrotreated Esters and Fatty Acids (HEFA), the latter representing a very high quality drop-in biofuel (suitable either for road transport or for aviation). However, extracting the algae oil at low cost and industrial scale is not yet a mature process, and there is not yet industrial production of algae-biofuel from these two lipid-based chains. Another option can however be considered: processing the algae through dedicated thermochemical reactors into advanced biofuels, thus approaching the downstream processing of algae in a completely different way than separation. The present work examines the possible routes for thermochemical conversion of microalgae into liquid biofuels, distinguishing between dry-processes (namely Pyrolysis, PO) and wet-processes (near critical-water HydroThermal Liquefaction, HTL). A literature review on algae-HTL was carried out, distinguishing between batch and continuous experiments, and compared to original results from algae pyrolysis. In particular, pyrolysis was carried out on both starved (lipid-accumulated) and non-starved microalgae. Typical composition of major products is given for both PO and HTL, comparing the main characteristic of the products.

Major engineering advantages and challenges in thermochemical conversion of algae into liquid biofuels were identified and discussed for both processes, in view of the production of a transport biofuel and the full exploitation of this renewable feedstock in energy and biorefinery complexes.

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* Corresponding author.
E-mail address: david.chiaramonti@re-cord.org (D. Chiaramonti).

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1. Introduction and scope of work

A large number of scientific works demonstrated that the production of biofuels from microalgae is technically feasible [1], even if not yet optimized: however, the achievement of a positive economical and energy balance is still under demonstration [2–4]. Today, as well as probably in the short/medium-term, biofuels from microalgae represent a niche area, with few existing commercial applications in non-energy sectors: nutraceuticals/functional foods, feed supplements, aquaculture, pigments, and polyunsaturated fatty acids, diagnostic and fine chemicals. Micro-algae market volume in 2004 was estimated equal to 5000 tons dry weight per year, accounting for 1 Bill.€ economic value [5] (i.e. 200 €/kg dry alga in average). Clearly, the conversion of algae to sustainable biofuels has not yet reached commercial level, despite the large potential offered by the algal feedstock. Among the main factors limiting the development of algae markets, especially biofuels and food, the most relevant ones are probably the biomass production and processing costs, mostly due to the complexity of the cultivation phase and the downstream processes required to extract the high-value products in a biorefinery concept. Despite these critical issues, and the actual light conversion (photosynthetic) efficiency, algae biofuels are particularly attractive thanks to the following major elements: (i) algae can be produced on marginal or degraded lands, avoiding competition with traditional food crops; (ii) algae are able to accumulate significant amounts of lipids (for biodiesel, HVO, and other processes) or carbohydrates (for bioethanol); (iii) algae can be grown without pesticides or herbicides; (iv) algae can grow in saline waters, thus without depleting fresh water resources; (v) algae can use carbon from flue gases; (vi) they can be cultivated on wastewaters, where algae can also find part of those nutrients needed to grow [6].

The development of an efficient microalgae-biofuel production pathway is still a major challenge toward commercial deployment, both from a strictly technical point of view as well as from an economic one. Despite the high biomass production of microalgae per unit of land ($t\ ha^{-1}$), energy consumption of biofuels from algae – including harvesting and extraction – is a major limiting factor for the economics balance and overall sustainability. The algae harvesting phase is responsible for a significant share of energy consumption and it can account for a 20–30% of the total production cost [7]. Downstream processing must separate very small cells (1–50 μm) from a cultivation medium characterized by a very low density of microorganisms (from 0.5 to $3\ gr\ l^{-1}$). Moreover, there is no optimal solution for algae harvesting and downstream processing, as each algae strain and product destination can set different technical specifications [8–10]. In fact, physical shape, cell wall structure, and microorganism composition can show significant variations even considering the same strain cultivated following just two different procedures. The selection of the harvesting method for a certain strain should be carried out taking into account the specific downstream process. As various authors agree, also the dewatering phase should be evaluated on the base of the following thermochemical treatment, so to achieve a proper operation and reducing overall energy consumptions [7,11].

The approach to downstream processing of microalgae toward biofuels and bio products can be very different. We can identify two major possible pathways:

- Microalgae are pre-processed, extracting the high added value compounds as lipids and/or carbohydrates, and then biofuels and biochemical are produced from the different fractions.
- The entire microorganisms are processed in the cultivation medium (wet processing), and bioliquids or intermediates are produced.

While carbohydrates are interesting for ethanol production, so far the lipid production for biodiesel has attracted the greatest interest: the potential oil yield per unit of used land of microalgae is 5–20 times higher that of palm oil (ton $ha^{-1}\ yr^{-1}$) [12,13].

In a lipid-based approach toward diesel-like biofuels, as biodiesel and HVO (Hydrotreated Vegetable Oils), specific cultivation techniques – such as Nitrogen and Phosphorous starvation can improve the oil quantity and quality toward downstream processes. In fact, depending on microalgae strain, removing nutrients (such as Nitrogen) from the growth medium reduces the cell division process, generating a "stress" effect that increase cell size and accumulate lipids, as observed in *Chlorella vulgaris* [14] and *Nannochloropsis* sp. Bondioli [15] showed that oil from starved *Nannochloropsis* sp. *F&M-M24* has suitable characteristics for biodiesel production: algae accumulated neutral lipids up to 50% of the dry biomass, with triglycerides representing the most abundant component. This algal oil – with the exception of a PUFA – mostly fulfills chemical requirements for a feedstock to be converted into biodiesel. However, lipids contained in microalgae are located intracellular: this makes the oil extraction significantly more complex than the extraction from conventional oil seeds, such as sunflower or rape. In fact, mechanical pressing is not applicable to microalgae [16]. After harvesting, the algae paste still contains more than 80% water (on wet basis): this is a key element for the selection of the following downstream processing methods. Wet extraction can thus be adopted in order to avoid biomass drying and therefore save energy, improving the overall sustainability [17].

However, dry extraction routes are today the more mature technologically options: moreover, they separate the protein-rich cake, a high added value co-products that contribute to improve the economic performances of the system. Chemical solvent extraction is the most common methods used to extract lipids from oily seeds: the efficiency of the solvent extraction process is strongly dependent on the specific algae strain under consideration [18].

Wet extraction has the important advantage of avoiding the drying step. In wet pathways, cell disruption can be based on mechanical approaches (e.g., microwave, ultrasonication, high pressure stresses, sudden changes of pressure, etc.), biological approaches (e.g., use of enzyme for cell disruption, osmotic stresses, etc.) or thermochemical processing (e.g. Hydro Thermal Liquefaction).

Among the biological extraction methods, enzymatic extraction degrades the cell wall, with relevant energy saving [19]. In fact, even if cell membranes of several microalgae (such as *Chlorella*) have very resistant layers, these can be degraded by the action of a proper mixture of enzymes [20]. The advantages offered by the enzymatic route are the mild reaction conditions and the high selectivity: compared with mechanical methods, enzymatic methods thus exhibit very competitive performances [21]. The critical element of this method is represented by the enzyme cost.

Hydrotreating can be economically competitive only if implemented at large scale. Efforts have been done even to retrofit existing refineries to HVO, with a first installation entered in operation in Porto Marghera, Venice.

Once the oil is extracted from the cells, the most diffused route toward biofuels is the transesterification process, which generates biodiesel, a mixture of Fatty Acid Methyl Esters (FAME). Biodiesel, which consists of "oxygenated" components, can be blended with fossil fuels only up to a certain percentage, and therefore subject to the so called "blend wall" (7% v/v in the EU). Actually, biodiesel exhibit several limitations, such as low oxidation stability, poor characteristic at low temperatures, and it becomes a solvent at higher blends. A way to overcome these limits, and to produce a very high

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